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Long Time-Scale Atomistic Simulations

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FY04 LDRD Final Report

Long Time-Scale Atomistic Simulations
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Abstract

During the past two years, we have succeeded in implementing an efficient parallel Importance Sampling Monte-Carlo (ISMC) scheme with application towards rarely occurring transition events, of great abundance in materials science and chemistry. The inefficiency of the standard atomistic modeling techniques for these problems may be traced to the extremely low probability of sampling system trajectories, or *paths*, that lead to a successful transition event. Instead of following the conventional approach of developing smart algorithms for searching transition paths, we tackle this problem by explicitly enhancing the probability of sampling successful transition events by means of an *importance function*. By selecting it appropriately, one focuses predominantly on the successful transition paths while discarding most irrelevant ones. In this manner, the rare-event problem is reformulated into an *optimization* problem for finding the best-possible importance function. Utilizing efficient iterative minimization algorithms, our IS approach can now be used to calculate the rate of occurrence of low-probability transition phenomena of short duration (short successful *paths*), but which involve collective degrees of freedom of many atoms. A detailed description of our methodology has recently been published in Journal of Chemical Physics **122**, 074103 (2005).

I. Introduction

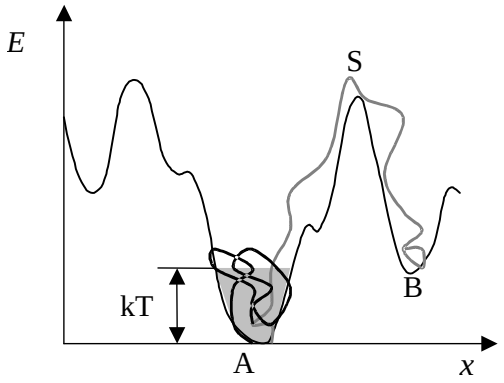

Fig. 1. *Origin of time-scale disparity: many-body system spends most of its time in deep energy basins, such as A. With an energy barrier much higher than the thermal energy kT, transitions between basins are very rare. The gray curve shows a typical transition path from A to B via saddle point S. It has a significantly lower probability than that of equilibrium paths that explore a single energy basin, such as the curve shown in black.*

Atomistic simulation has become an indispensable tool in many fields of research, including chemistry, physics, biology and materials science, where a fundamental understanding of how unit mechanisms control the macroscopic behavior of complex systems is needed. Unfortunately, standard atomistic simulation techniques [1], such as Molecular Dynamics (MD) and Monte Carlo (MC), are severely limited in the length of time interval during which the processes of interest can be followed. This key limitation stems from the fact that MD and MC naturally operate on time scales of typical atomic vibrations in the system. For example, in solid-phase systems this scale is defined by a characteristic phonon frequency, typically of the order of 10^{13} Hz. Accordingly, the maximum simulation time accessible to current atomistic simulations is only of the order of nanoseconds. Yet, many phenomena of interest occur on time scales of milliseconds and longer, e.g. relaxation in glasses and protein folding, and remain totally out of reach for present-day MD and MC techniques.

This time-scale disparity can be traced to certain topographical features of the potential-energy surface that characterizes the interactions in the many-body system [2]. Often, the system spends most of its time in deep energy basins surrounded by energy barriers that are many times larger than its thermal energy. Only very occasionally, thermal fluctuations allow transitions over the barriers and movement to the neighboring basins, as shown in figure 1. Given that the transition rate decreases exponentially with increasing barrier height, such transitions represent rare events on the time scale of atomic/molecular motion. Consequently, attempts to simulate

them directly using MD or MC are hopelessly inefficient, since virtually all CPU time is spent on the "irrelevant" equilibrium motion within a basin. Given that the disparity in time scales can be so large, not even petaflop scale computing can close this gap in the foreseeable future. Hence, development of smart simulation techniques remains the only hope for studying rare-event processes at the atomistic level. Unfortunately, the current state-of-the art techniques have yet to offer a satisfactory solution, with most methods suited only for relatively simple transitions involving few degrees of freedom.

II. The Idea: Importance Sampling of Paths

The time-scale disparity problem in atomistic simulations can be formulated in terms of a probability distribution function of system trajectories or paths. In this context, a rare event is characterized by an extremely low probability for sampling a transition event, compared to that of generating an unsuccessful path. The standard simulation techniques (MD and MC) generate paths according to their natural probability distribution function, and are hence extremely inefficient, spending virtually all CPU time on sampling "irrelevant" equilibrium paths while waiting for a transition event to occur. Therefore, a comprehensive solution to the rare-event problem in complex systems should be based on a statistical description of the ensemble of system paths.

In this context, a successful approach would be to modify the standard MD and MC techniques in such a manner that the probability of sampling a successful transition event is enhanced while spending less CPU cycles on the "irrelevant" equilibrium trajectories. A good *importance sampling* (IS) scheme of this kind should satisfy two conditions: (i) the *relative* probabilities of different transition trajectories must remain unaltered, and (ii), the absolute probability of sampling a successful transition event should be enhanced by a *known* amount. These two conditions should be met in order to ensure that different transition mechanisms are sampled with correct relative probabilities, and to allow a straightforward calculation of the corresponding transition rates.

With these two requirements in mind, our idea to approach this problem is based on enhancing the probability of sampling successful transition events by using an *importance function*. By selecting it appropriately, one focuses predominantly on the successful transition events while keeping track of the quantitative changes in their absolute probabilities. In this manner, the rare-event problem is reformulated into an *optimization* problem for the best-possible importance function. Once this function is known, the problem is solved completely: only successful transition events are generated while *all* others are suppressed. In addition, since the probability of generating successful paths is modified by a known amount, the transition rates can be readily obtained.
This idea was implemented and tested on simple low-dimensional rare event problems and was found to be very successful [3]. In particular, we designed an automated numerical procedure for identifying the *optimal* importance function, which maximizes the sampling efficiency of rare transition events. The central goal of this proposal is thus to see whether we can apply this general idea to complex many-dimensional systems, for which finding an optimized importance function presents a non-trivial challenge. With the important progress made in FY03 and FY04, we are in a good position to believe that this idea is working. Specifically, we have successfully developed an efficient, order N, parallel, importance sampling Monte Carlo algorithm for realistic many-atom systems and applied it to materials science problems of defect migration in solids.

IV. Accomplishments

In FY03 we succeeded in extending the applicability of our IS approach [3], to a realistic problem involving large number of degrees of freedom, i.e. the case of dislocation motion in silicon. We had chosen this problem for mainly two reasons: (i) it is an important transition event in crystals that involves collective motion of many atoms, but (ii) nevertheless the number of the important degrees of freedom in this problem is rather few. Hence by choosing a few-dimensional importance function we hoped to solve this multidimensional problem. For this purpose we devised a new general-purpose iterative optimization algorithm that is well suited for searching for the optimal importance function in arbitrary spaces. The result of this work was an importance-sampling scheme capable of treating a limited range of realistic problems, and most importantly a method for estimating the statistical error in our calculated transition rates was now in place.

The overall result of our work in FY03 was very encouraging but it also introduced some new problems. Two specific stumbling blocks were: (i) large fluctuations in the calculations for non-optimal importance functions, and

(ii) the functional optimization procedure for even simple importance functions in realistic systems becomes computationally very expensive. Another limitation of our method was that we had applied the IS approach by choosing the functional form of our importance function using prior knowledge of the geometry of the dislocation motion in silicon. It is worth mentioning here that each one of the issues mentioned above are quite formidable problems, and no general solution have ever been put forward for any of them.

In FY04, we tried to tackle all the issues alluded to above. We made several innovations that have led to breakthrough progress in the applicability of the IS approach. We have also implemented a very efficient ISMC code package for parallel environments that will be used as a basis for all future developments. We have published a detailed account of our methodology and accomplishments in the *Journal of Chemical Physics* [5]. Below follows a brief technical summary.

1) Development of new importance sampling methodology

When performing Monte Carlo simulations for a system of N atoms, it is common practice to perform trial moves for one atom at a time. This is achieved by choosing an atom at random with a uniform probability distribution. In this way the computational cost of moving all the atoms in the system by one step scales as $O(N)$. In FY03, we implemented an IS approach based on this approach. However, we found that when certain degrees of freedom are singled out as more important than others, this algorithm leads to extra fluctuations. It worth noting, that this is a common problem encountered whenever ISMC simulations are performed. In our case, this problem is even more noticeable, since we are using MC to perform functional optimization of the importance function itself.

To remedy this age-old problem, we have invented a modification of the IS algorithm where we choose each trial move from the correct probability distribution that is calculated at each simulation step. Such simulations in general lead to an $O(N^2)$ computational cost per step. Our main contribution has been to implement this feature with an algorithm that scales as $O(N)$ per step. This innovation has reduced the fluctuations in our calculations by orders of magnitude. This has allowed us to reach breakthrough success in reducing both the computational cost and error of our calculated rates dramatically.

2) Implementing efficient optimization algorithms.

In FY03, we devised an IS functional optimization scheme, where given a parametrized functional form for the importance function, a variational principle for a cost measure is formulated, minimization of which leads to the best possible importance function. This procedure was designed in analogy with the variational Quantum Monte Carlo methodologies [4]. In our case, the observable is the statistical weight of each path generated in an IS simulation. It can be shown that only when the *optimal* importance function is used, *all* simulated paths have the *same* weight (i.e, zero variance). For *any* non-optimal function, the path weight will vary from one path to the other. The variance in the path weights therefore represents a quantitative measure of the quality of the used importance function and is an appropriate cost measure for the parameter optimization. In FY03, the parameters were optimized through an iterative steepest descent algorithm. While very crude, we were able to obtain good importance functions in FY03. At the same time, we also observed some of its limitations, such as its sensitivity to the initial guess of the parameters as well as the magnitude of the steps taken along the force direction. For this purpose, we have completed a comprehensive investigation of various more elaborate functional minimization schemes, in particular genetic algorithms (GA). We have found that great gains can be made, when suitable minimization technique, as well as cost measure is used.

3) Construction of a parallel and efficient general-purpose ISMC program package.

In order to be able to tackle larger problems, we have implemented a fully parallel version of our ISMC technique, which has allowed us to make accurate error estimations, a very important ingredient for assessing the quality of the different algorithms. Our aim was to implement a flexible and parallel program package that performs ISMC simulations to search for transition barriers for e.g. defect diffusion in solids and chemical reactions. Almost all this work has been performed on the same model problem, i.e. the dislocation kink motion in silicon, based on the Stillinger-Weber potential.

However, we have also worked on extending the applicability of our method to other interatomic potentials, such as EAM, as well as multicomponent systems and alloys. As a result, we have now the unique capability of performing

linear-scaling parallel Monte Carlo simulations of configurational as well as topological entropy of multicomponent alloy systems.

4) Exploring variance reduction methods

We have also explored some other techniques to further reduce the variance and increase the accuracy of our calculations. In particular, we have managed to implement the Prune-enriched Rosenbluth Method (PERM) within our IS approach. This is an alternative Monte Carlo method that has been very successful in the past in finding the ground state of e.g. various lattice polymer models.

5) Beyond low-dimensional importance functions: the way to the future

We believe that our technique can be applied to more complex transition phenomena, such as nucleation and growth in first-order phase transformations. For this purpose it is important to extend our IS approach to problems where prior physical knowledge is not available. For a system of N atoms, this implies that we need to work with the a $3N$-dimensional importance function. This means an exponential growth of computational complexity, as the number of degrees of freedom is increases. This is of course a general problem encountered by anyone working in this field.

We have recently invented a systematic approximation to the exact optimal importance function by decomposition into $O(N)$ few-dimensional functions. We have implemented several different functional forms of this kind during FY04, where $O(N)$ one-dimensional functions have been summed to obtain the total importance function. Note that the success of this attempt would imply a reduction of a problem with exponential complexity to an $O(N)$ problem. On the date of writing this text, we are just about finished with our first implementations of these ideas. We are quite hopeful that we will be able to apply these ideas to very complex problems in statistical mechanics.

6) Modeling Martensitic phase transformation

With the fundamental methodological elements in place, we have started working on the specific problem of the FY04 Milestone, the simulation of a martensitic structural transformation. For this purpose we have implemented a very recently developed, many-body interatomic potential for titanium, one of the most interesting transition metals, with a polymorphic phase diagram. At ambient temperatures and pressures this system is found in the hcp phase. Upon pressure it undergoes a phase transformation to a complicated structure, the so-called omega phase. At high temperatures the bcc-Ti is the thermodynamically stable phase. We have established the accuracy of this potential by studying the dynamics of a shock-induced phase transformation in Ti. This study has led to very promising and important results. We can observe an unprecedented three-wave shock front where the initial alpha-Ti structure (hcp) becomes plastic and subsequently undergoes a transition to the Ω phase, and further to the bcc phase. This simulation is the first of its kind, and provides an invaluable source for exploring the kinetics of structural phase transformations. In addition the results that we have obtained until now, are in excellent agreement with the available experimental data.

Of course, strong shock waves can allow for phase transformations to occur on the time scales accessible to computer simulations. However, when the driving force is weaker, the phase transformations are much slower and straightforward molecular-dynamics simulations are not possible. With the IS methodology developed so far, and the results already obtained from our non-equilibrium shock simulations, we are well-positioned to take on the problem of martensitic transformations in solids occurring over long time scales.

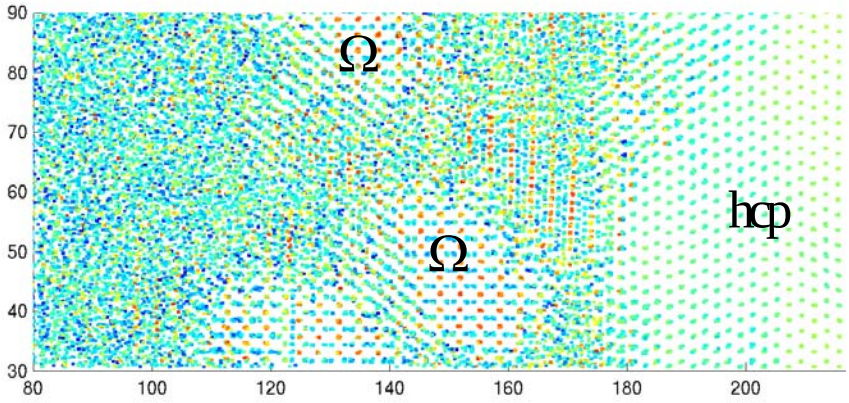

Fig 2. Cross-sectional view of a shock wave traveling through Ti, causing a phase transformation. The maximum pressure is 40GPa, and the piston is on the left of the figure moving at 1.5km/sec into a cold initial sample. The region near 200Å is the untransformed hcp Ti; and the omega phase is in the region around 160Å on the x-axis. The coloring is based on the average coordination of each atom obtained using Voronoi cell decomposition. The blue color indicates 10 fold coordinated atoms, green 12, and red 14.

V. Exit Strategy

Completion of this two-year research plan has established a solid theoretical and practical foundation for long-time-scale simulations of complex many-body processes in materials science and chemistry. This will constitute a major advance in our ability to model and understand many fundamental processes that are of critical importance to several large programs at LLNL, such as metal plasticity and materials aging. Combining our methodology with the existing simulation expertise and the unique computational facilities at the Laboratory will significantly enhance our predictive atomistic modeling capabilities. We believe that our activities will engender continuing support from other funding sources. To this end we are applying our methodology to problems such as martensitic phase transformations, defect diffusion in solids and chemical reactions.

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